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Synthesis of nanoencapsulated Glauber's salt using PMMA shell and its application on cotton for thermoregulating effect

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Abstract

Phase change materials (PCM) are capable of storing thermal energy and can be used in smart textiles providing thermoregulating effect. Different PCM stores different amount of energy at certain temperature and then release the stored energy in the form of latent heat. This research reports the synthesis of nanocapsules containing Glauber's salt as a core PCM and its characterisation using differential scanning calorimetry and scanning electron microscopy. The cotton fabric was treated with synthesized nanoencapsulated Glauber's salt via pad-dry-cure process and was characterized using DSC and SEM in comparison with commercial microcapsules. The synthesized capsules of Glauber's salt were found in the range of nano scale around 500 nm on average. The DSC results indicated that the nanoencapsulated Glauber's salt showed better results after they applied on fabric and does not wash off easily. The novel nanocapsules developed and reported in this article will establish a better understanding of PCM to use in different field of material science. This research will effectively exploit the potential use of encapsulated Glauber's salt in the field of material science such as smart cellulosic textiles.

Keywords

Nanoencapsulation, phase change materials, Glauber's salt, thermal analysis, cotton

Introduction

Phase Change Materials (PCMs) are organic or inorganic compounds which store energy upon melting and release it when solidifies. PCMs store large amount of energy by changing their phase at nearly constant temperature (Kürklü 1997). More than 500 natural and synthetic PCMs are known which differ in their melting temperatures and latent heat (Pause 2002), among the most suitable for textiles are n-octadecane and Eicosane with their phase change temperature of 28 °C and 37°C respectively (Zuckerman et al. 2003).

Because of the nature of PCMs, they cannot applied directly on textiles and need to be kept in protective reservoir (Mondal 2008). Thus the PCMs are encapsulated within the shell and these capsules are synthesized in the range from nanometres to micrometres and this process is called microencapsulation. The microcapsule is a reservoir in which the active substance is within the core and surrounded by a polymeric wall or shell. Green and Schleicher used this technique for the first time in 1950 for carbonless copying paper(Arshaday 1990). This microencapsulation technique was further utilised on lab scale in 1990 and applied on industrial scale later on for value added textile materials (Nelson 2002).

The nanoencapsulation of PCM under 1μm size (Sarier and Onder 2012) exploit many techniques of encapsulation such as simple and complex coacervation (Uddin et al. 2002), *in-situ* polymerisation (Jin et al. 2008), interfacial polymerisation (Chen et al. 2012) and spray drying (Borreguero et al. 2011). The most commonly techniques are in-situ polymerization and solvent evaporation method (Borreguero et al. 2011; Hawlader et al. 2003; Hawlader et al. 2000; Teixeira et al. 2004). The capsules of PMMA (polymethyl methacrylate) shell are developed by the technique solvent evaporation while melamine formaldehyde shells are synthesized using in-situ polymerization. (Mondal 2008; Zhao and Zhang 2011)

Shin et al. (2005) encapsulated n-eicosane and Sarier and Onder (2007) encapsulated octadecane and eicosane as core material using melamine formaldehyde and urea formaldehyde as shell material respectively by *in-situ* polymerisation. They found the latent heat of 134.3 J/g of microcapsules with capsule size less than 2 μm. They applied prepared capsules on textile and determined the latent heat of 4.44 J/g for the treated textiles. Many researchers prepared encapsulated phase change materials composed of different shell and materials using different techniques such as Fang et al. (2010) prepared paraffin PCM with silicone shell via Sol-Gel method, Li et al (Li et al. 2011) synthesized PCM using urea formaldehyde shell. Salaun et al. (2010) synthesized capsules using M/F with mixture of paraffin along with additive to enhance latent heat. Sánchez et al. (2010) developed microencapsulated paraffin from C_{19} to C_{27} as a mixture in the range of 40 to 45 °C using polystyrene as shell material. They found 7.6 J/g of latent heat after the application on 100% cotton fabric.

Many researchers are paying attention to nanotechnology now a days because of the enhanced surface characteristics due to the nano size and they produced best results after application on textiles (Sarier and Onder 2012).

Nanocapsules with PMMA as shell material and paraffin within the core for thermal energy storage have been synthesized by many researchers such as Sari et al. (2009), Kwon et al. (2010) and Black et al. (2010). They synthesized nanocapsules ranging particle size from 100 nm to 280 nm. Alay et al. (2010) encapsulated n-hexadecane using PMMA shell and found the nanocapsules average size around 260 nm with 148.05 J/g of latent heat. This latent heat after the incorporation into electro spun PAN fibre was measured as 36.80 J/g.

Glauber's salt which is chemically Sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) is used as PCM and is very attractive due to its high amount of latent heat of 254 J/g, high thermal conductivity and lower cost than other phase change materials such as paraffin. The phase change temperature of Glauber's salt is 32.4 °C and this temperature is closer to the skin comfort temperature (Canbazoğlu et al. 2005). Hydrated inorganic salts have capacity to store large amount of energy due to its decahydrate water of crystallization (Saito et al. 2001). The content of water of crystallization was studied and investigated by Biswas (1977) and Marks (1980) and was found to be 56% of the Glauber's salt.

The nanoencapsulation of Glauber's salt has become a challenge because of their high water solubility and difficult to get encapsulated. Their synthesis as nanocapsules for the application on cellulosic textiles has not been reported yet in the literature. They are really attractive energy storage materials for all type of application specially textile materials as their phase transition temperature is closer to human skin temperature. Also their latent heat is more than paraffin while market price is much less than paraffin. This research focuses on the synthesis of nanoencapsulated Glauber's salt and their application on textiles for thermoregualting effect.

Materials and Methods

For the preparation of PMMA shell, MMA (methyl methacrylate) and EA (ethyl acrylate) were used as monomer and purchased from Alfa Aesar®. The solvents used were toluene and dichloromethane purchased from Rathburn Chemicals and Fisher Scientific respectively. The inorganic Glauber's salt ($Na_2SO_4.10H_2O$) was used as phase change material and was purchased from Alfa Aesar®. Dibenzoyl peroxide (wet with 25% water), 4-methoxy phenol were used as reaction initiator and inhibitor respectively and both were purchased from Alfa Aesar®. Sodium polyacrylic acid was used as reaction stabilizer and was purchased from Sigma Aldrich. Tween® and polyvinyl alcohol were used as emulsifier and emulsion stabilizer respectively.

Encapsulation methodology

Solvent evaporation method was explored for the encapsulation of Glauber's salt and the procedure adopted is shown in Figure 1.

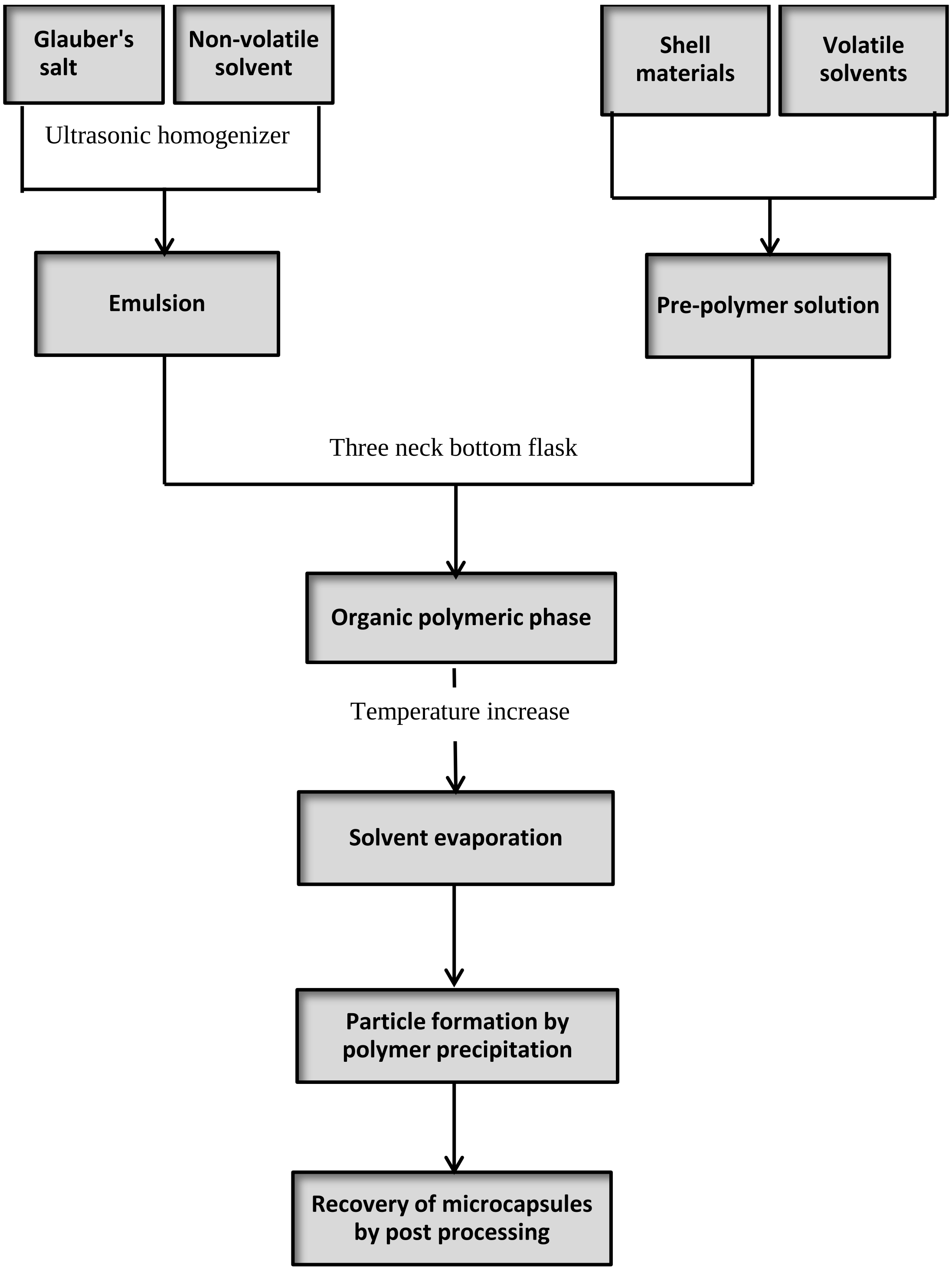

Figure 1 solvent evaporation technique for nanoencapsulation of Glauber's salt (Iqbal 2016)

Experimental

Encapsulation procedure

For the preparation of Glauber's salt emulsion, 20g of Glauber's salt was added in an organic solvent containing 80ml of toluene. 0.5g of emulsifying agent was added using ultrasonic homogeniser for 3-5 min at 30 °C until the emulsion is prepared. The emulsion was further stabilized by adding 5mg of PVA. The prepolymer solution was prepared by adding 12g of MMA and 2g EA in a 50 ml dichloromethane which is volatile solvent. This prepolymer solution was stirred at room temperature until clear solution was obtained. From the whole emulsion, half was poured into the round bottom flask and the solution of prepolymer was dripped into the emulsion with the help of splitting funnel. After that the reaction ingredients were added such as initiator and stabilizer while initiator was added in two portions for controlled polymerization reaction. The temperature was increased gradually and the rest of the emulsion was added in a flask at 60°C with stirring rate of 600 rpm while temperature was raised up to 80°C until the solvent was evaporated. The polymerization reaction was stopped by adding the inhibitor and sample was filtered, washed and dried. The washing was done with distilled water couple of times followed by diethyl ether and drying temperature was maintained at 40°C. The purpose of washing was to remove any unreacted species including none capsulated Glauber's salt.

Reaction mechanism

The polymerization reaction of MMA to form PMMA in the presence of initiator is shown in Figure 2. Figure 3 shows the free radical polymerization reaction between MMA and EA resulting in modified PMMA. The reason to use ethyl acrylate is because of its reactive nature and more prone to initiate reaction due to the presence of ethyl group which helps to propagate the polymerization reaction.

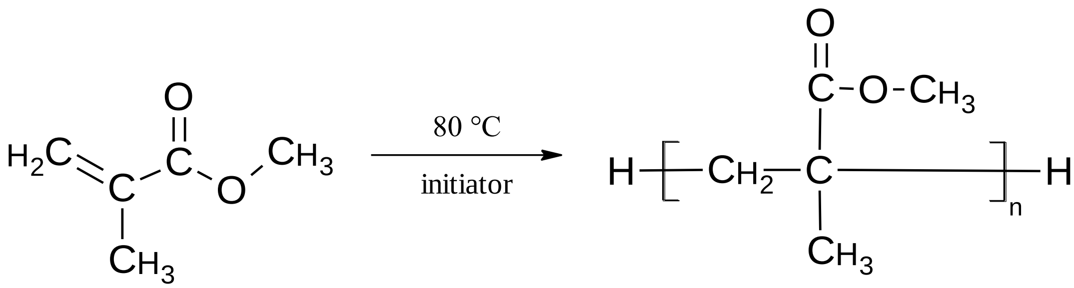

Figure 2 polymerization reaction of MMA to PMMA

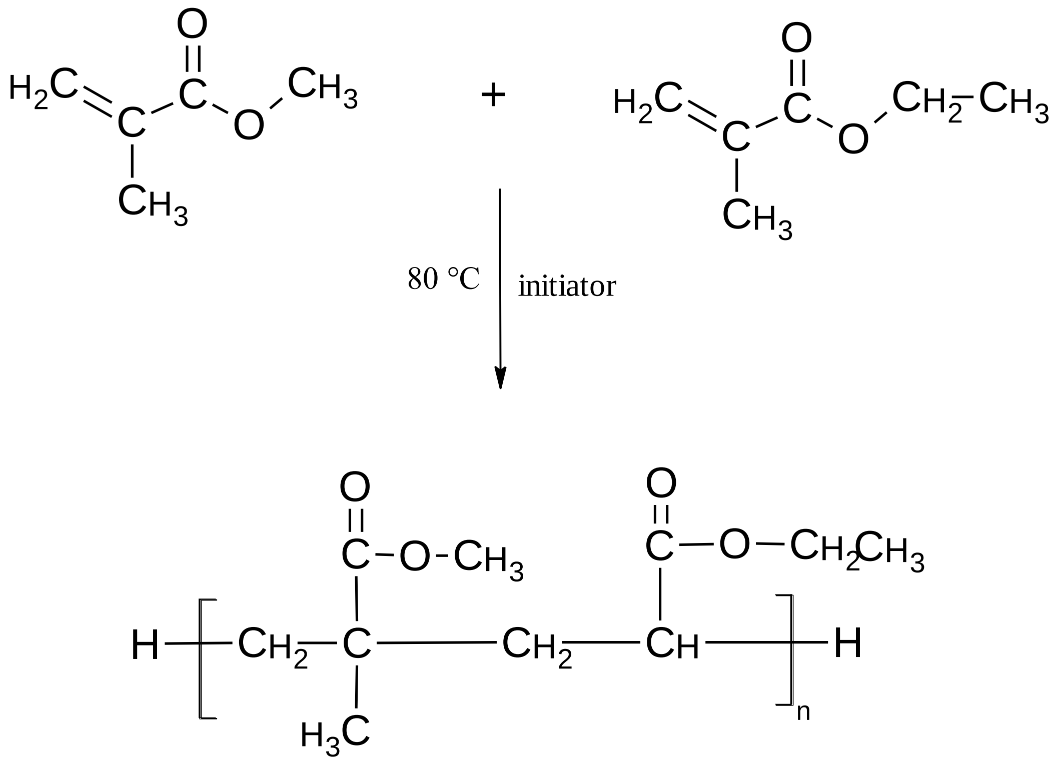

Figure 3 polymerization reaction of modified PMMA

Characterisation of nanocapsules containing Glauber's salt

Scanning electron microscopy

The SEM micrographs are shown in Figure 4 & 5. Figure 4 shows the image of nanoencapsulated Glauber's salt before washing in which the capsules seem agglomerated within the resin. Figure 5 shows the images of nanocapsules after washing with diethyl ether and the capsules are no longer agglomerated.

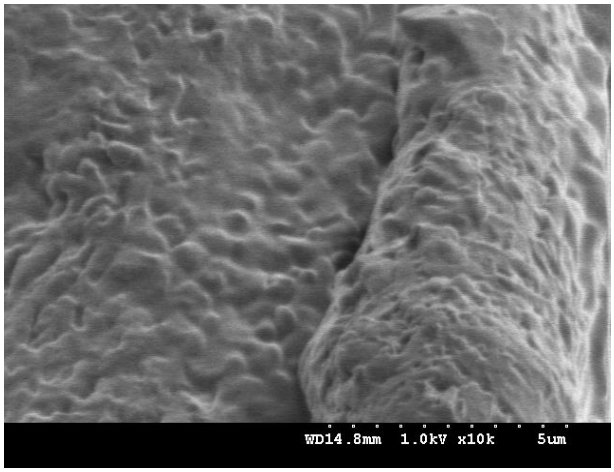

Figure 4 Synthesized nanoencapsulated Glauber's salt before washing

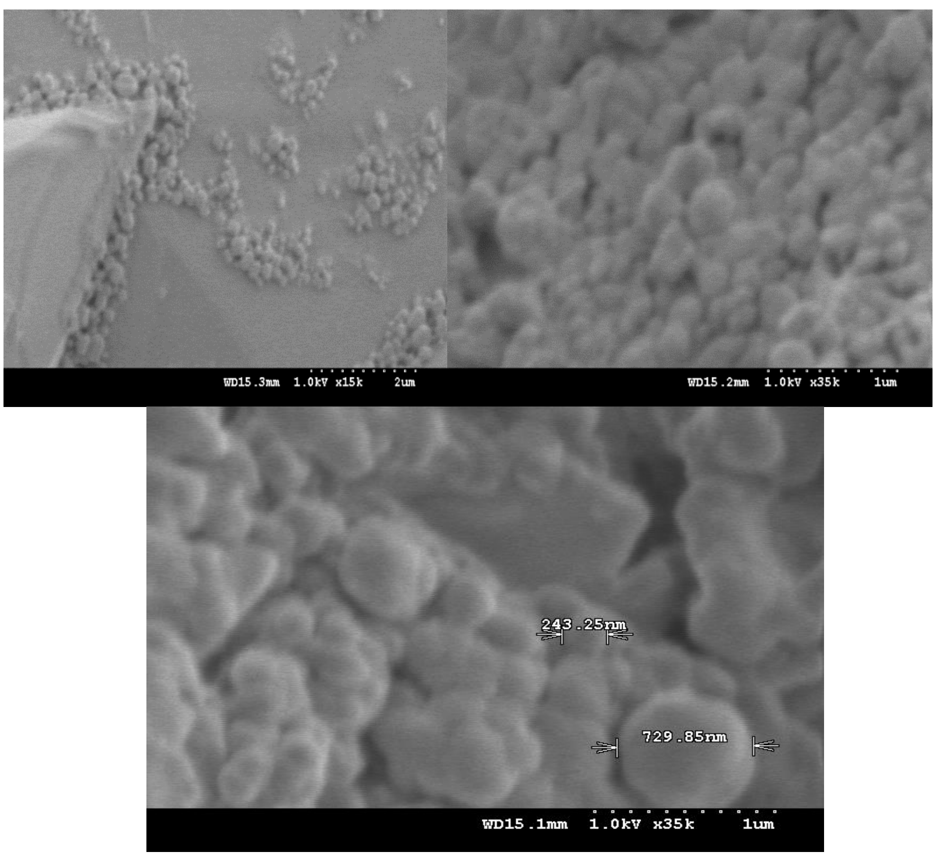

Figure 5 synthesized nanoencapsulated Glauber's salt after washing

DSC study of nanoencapsulated Glauber's salt

The latent heat of nanoencapsulated Glauber's salt was determined using differential scanning calorimetry. Figure 6 shows the DSC graph indicating the phase change temperature of encapsulated salt. The melting range has been shown by two perpendiculars around the peak starting at 32.4 °C and ending at 41.1 °C.

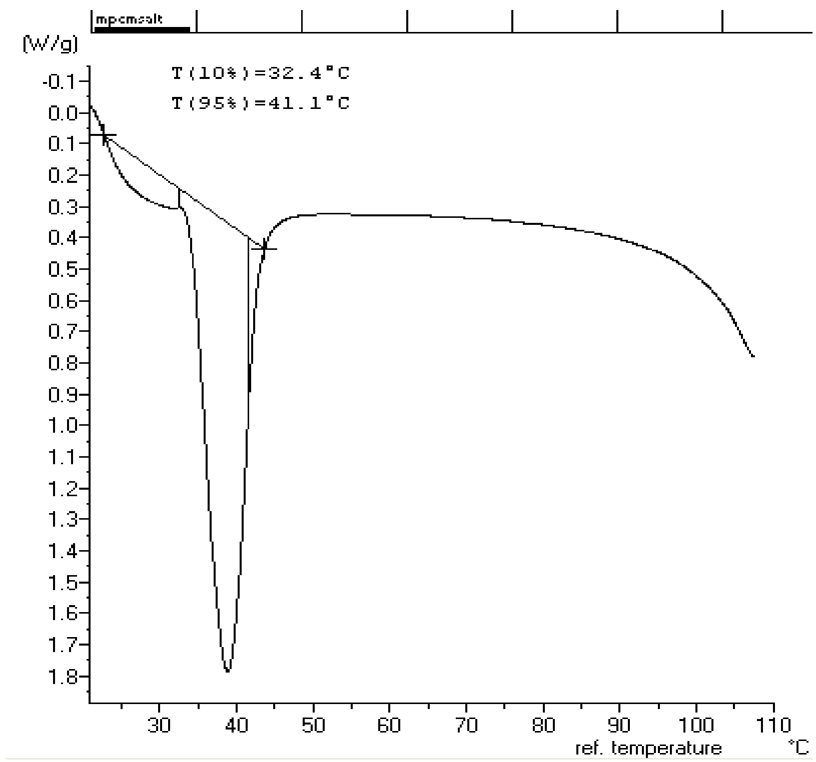

Figure 6 DSC graph showing latent heat of nanoencapsulated Glauber's salt

Figure 7 shows the DSC graph of nanoencapsulated Glauber's salt indicating enthalpy of PCM. The latent heat of 127 J/g was determined using differential scanning calorimetry which indicates a good amount of stored energy during phase change at the temperature range from 30 °C to 40 °C.

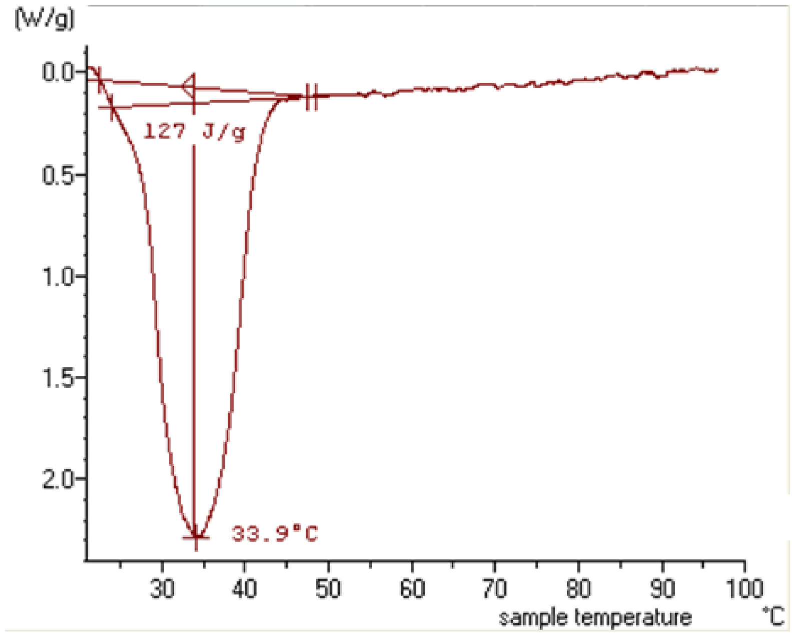

Figure 7 Enthalpy of nanoencapsulated Glauber's salt

Structure of nanoencapsulated Glauber's salt

FTIR image of nanoencapsulated Glauber's salt is shown in Figure 8. The confirmation of hydrated salt can be done by the existence of –OH group as shown in the absorption band at 3400-3550 cm^{-1}. A very much wider peak shows the bonded –OH group in the water of crystallization attached with Glauber's salt. The presence of $SO_4^{=}$ group in Glauber's salt is shown by the broader peak at 1060-1100 cm^{-1}. This peak with high intensity shows that the Glauber's salt is present and protected in a shell otherwise it could wash away during washing of nanocapsules sample. The presence of acrylate carboxyl group is shown by the band at 1750 cm^{-1}. The peak before 3000 cm^{-1} around 2800-2900 cm^{-1} shows the C-H stretching vibration and the existence of Sp^3 hybridised $–CH_3$ and Sp^2 hybridised $–CH_2$ groups. The peak at 2100 cm^{-1} can be attributed to the ethyl group $CH\text{-}CH_2$ stretching vibration of PMMA. All these functional groups show that the IR spectrum confirms the synthesis of nanocapsules with PMMA shell and Glauber's salt as core material.

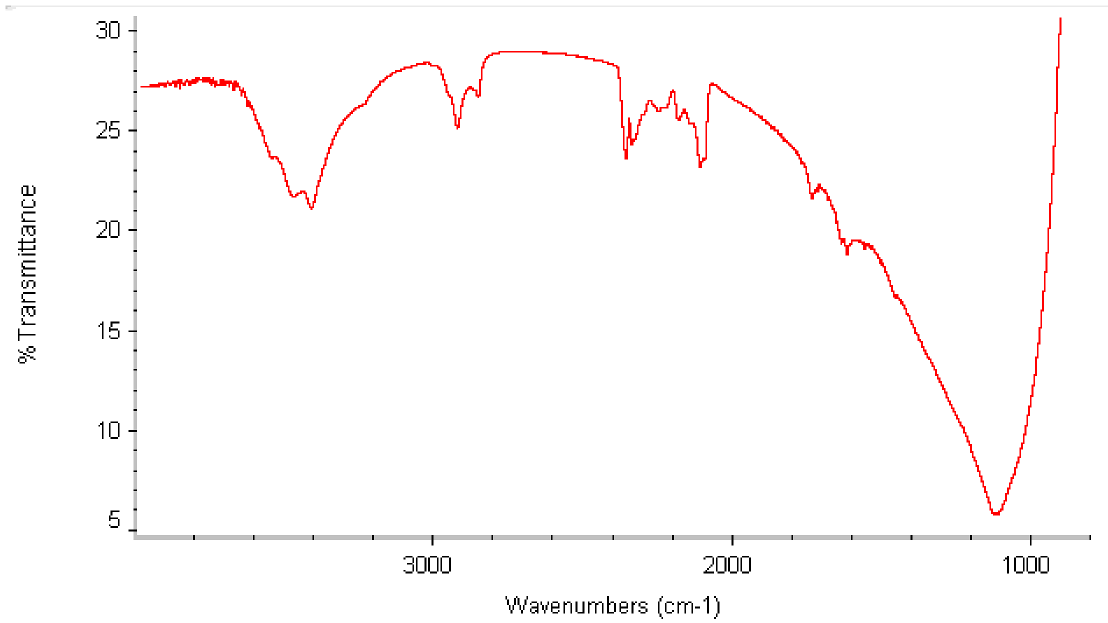

Figure 8 FTIR graph of nanocapsules showing chemical groups

Pad application of nanoencapsulated Glauber's salt on fabric

The nanoencapsulated Glauber's salt was applied onto plain woven fabric made of 100% cotton with the help of binder through pad-dry cure technique. The padding liquor contained 60 g/l of ARRISTAN EPD (urethane binder), 50 g/l of REAKNITT ZF (formaldehyde free cross linking agent), 50g/l of TUBINGAL RGH (modified silicone softener) and 8 g/l of CHT CATALYST AD, the recommended reaction catalyst, and 30% of nanocapsules on the weight of binder. The fabric was padded, dried at 110 °C and cured at 150 °C.

Each sample was characterized using SEM and DSC before and after one and 5 washings. The washing was done according to BS EN 26330.

Scanning electron microscopy of treated fabric

The images of cotton fabric after the application of NPCM Glauber's salt are shown in Figure 9. The images clearly indicate the nanocapsules on yarn or fibres attached with the help of binder. This Figure 9 shows the images of treated fabric before washing while Figure 10 shows the images of nanoencapsulated treated fabric after one wash. The capsules are still on the fibre or yarn at micro level as they are attached to the substrate with the assistance of crosslinking binder.

The thermal stability required in cellulosic textiles' application is judged by its application via pad dry cure method. Hence the SEM results of treated cotton fabric also indicate that nanocapsules were thermally and mechanically stable enough to bear the pressure of padder rollers and curing temperature of 150 °C suitable for the processing of cellulosic materials.

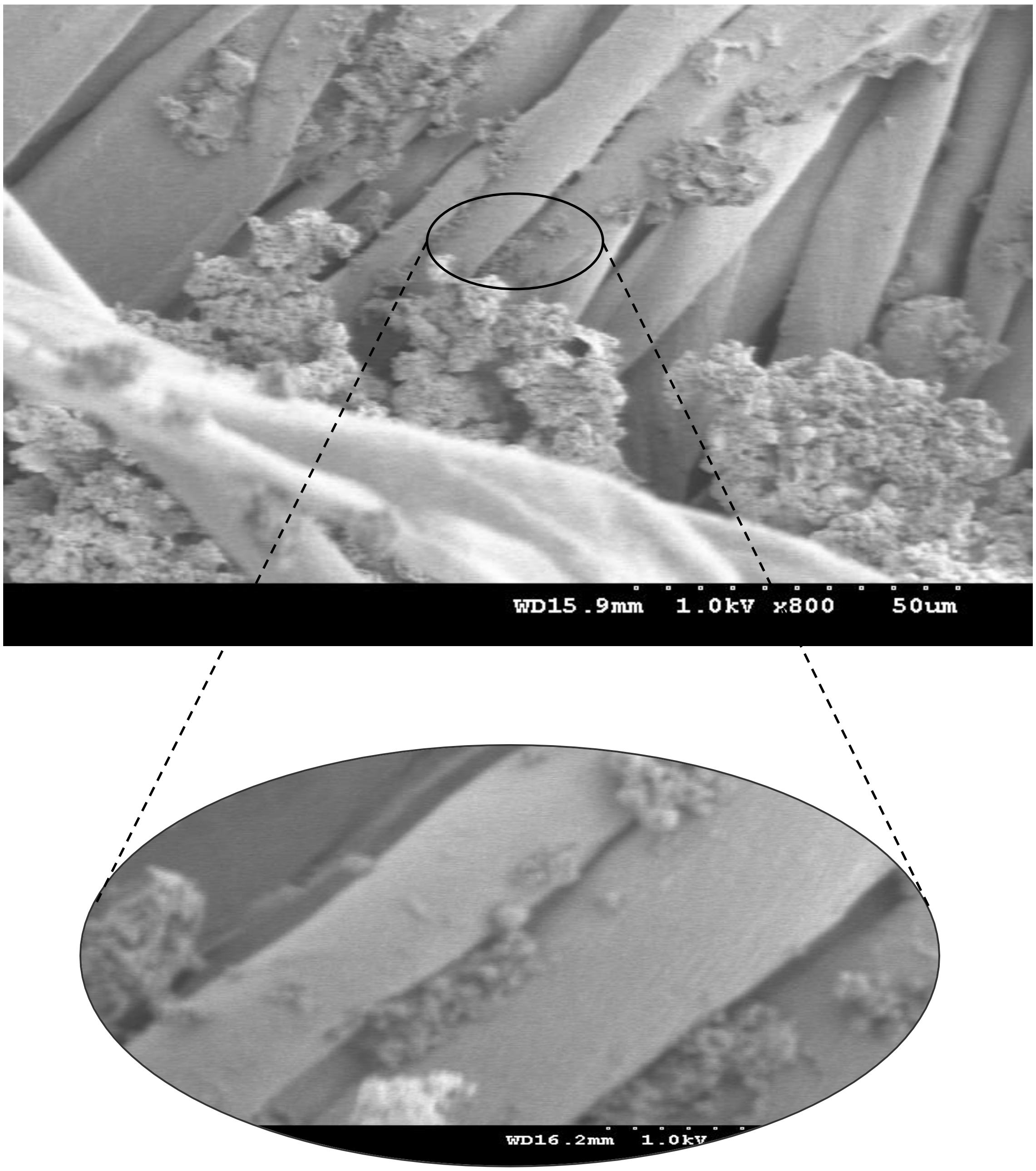

Figure 9 Nanoencapsulated Glauber's salt treated fabric before washing

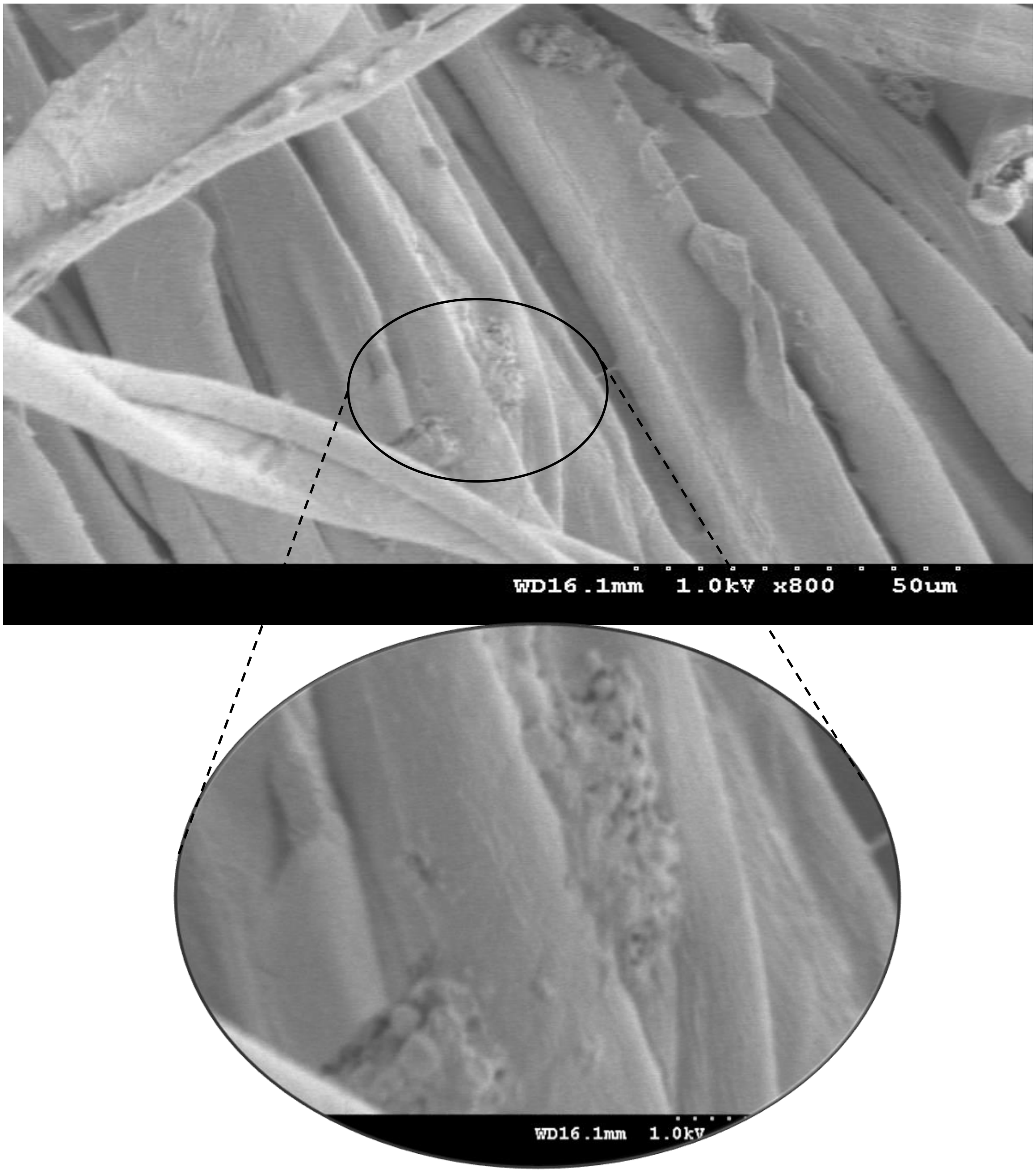

Figure 10 Nanoencapsulated Glauber's salt treated fabric after one wash

As the number of washings increase, the amount of nanocapsules decreases due to severe washing but still remain at micro or nano level as shown in Figure 11. The images are shown at higher magnification and indicate that the capsules in the nano range firmly attach themselves with the fibre and become the integral part of the substrate even after quite number of washings. Only those capsules are removed who are not strongly attached to the fibre and are deposited on the surface.

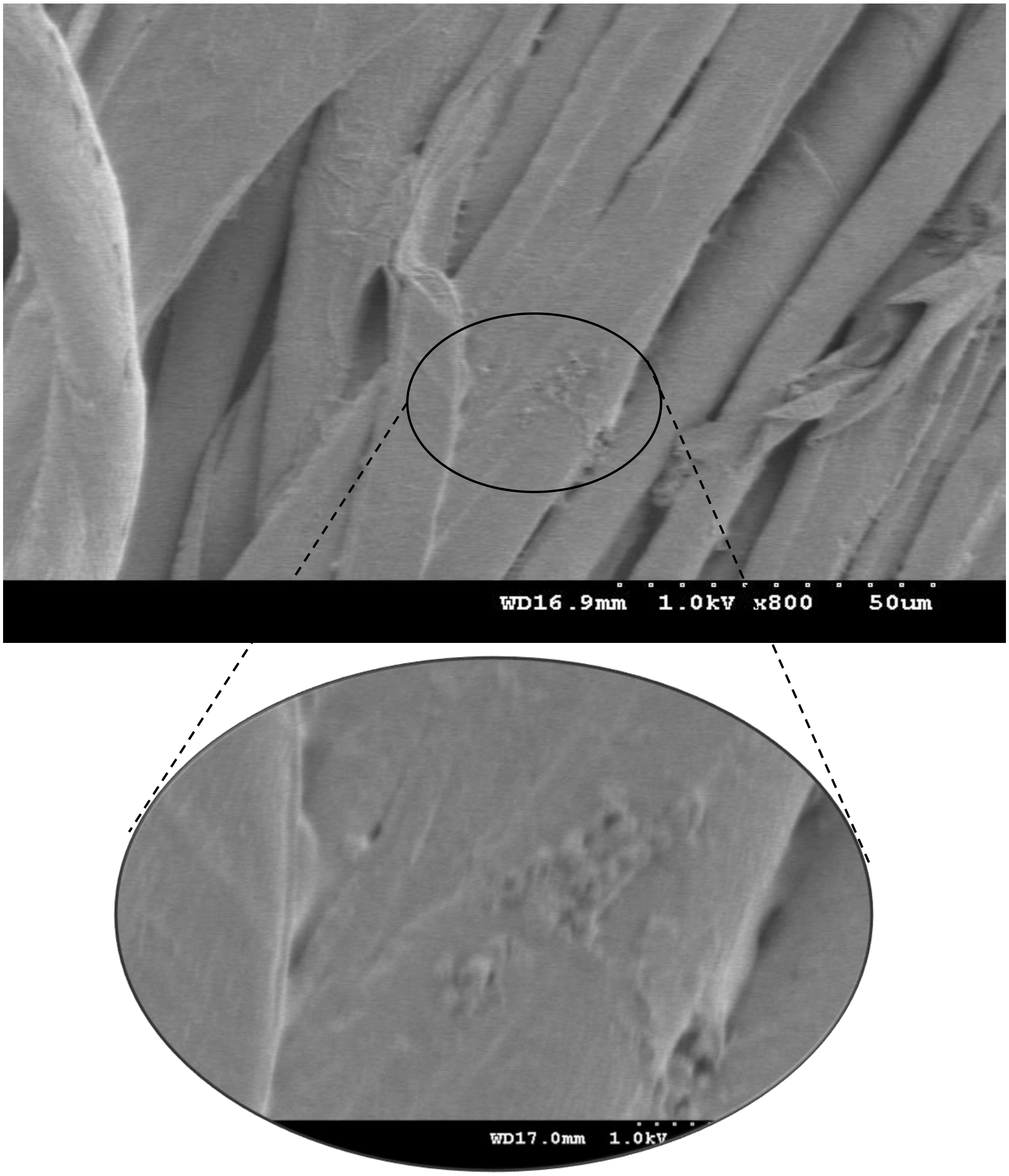

Figure 11 Nanoencapsulated Glauber's salt treated fabric after five washings

DSC study of treated fabric with nanoencapsulated Glauber's salt

The fabric treated with nanoencapsulated Glauber's salt was characterized using differential scanning calorimetry to obtain the values of latent heat of the treated fabric. DSC results showed 12.3 J/g of latent heat for treated fabric which decreased to 24.3% and 62.2% after 1^{st} and 5 washes respectively. DSC graphs are shown in Figure 12 indicating the latent heat before and after washing.

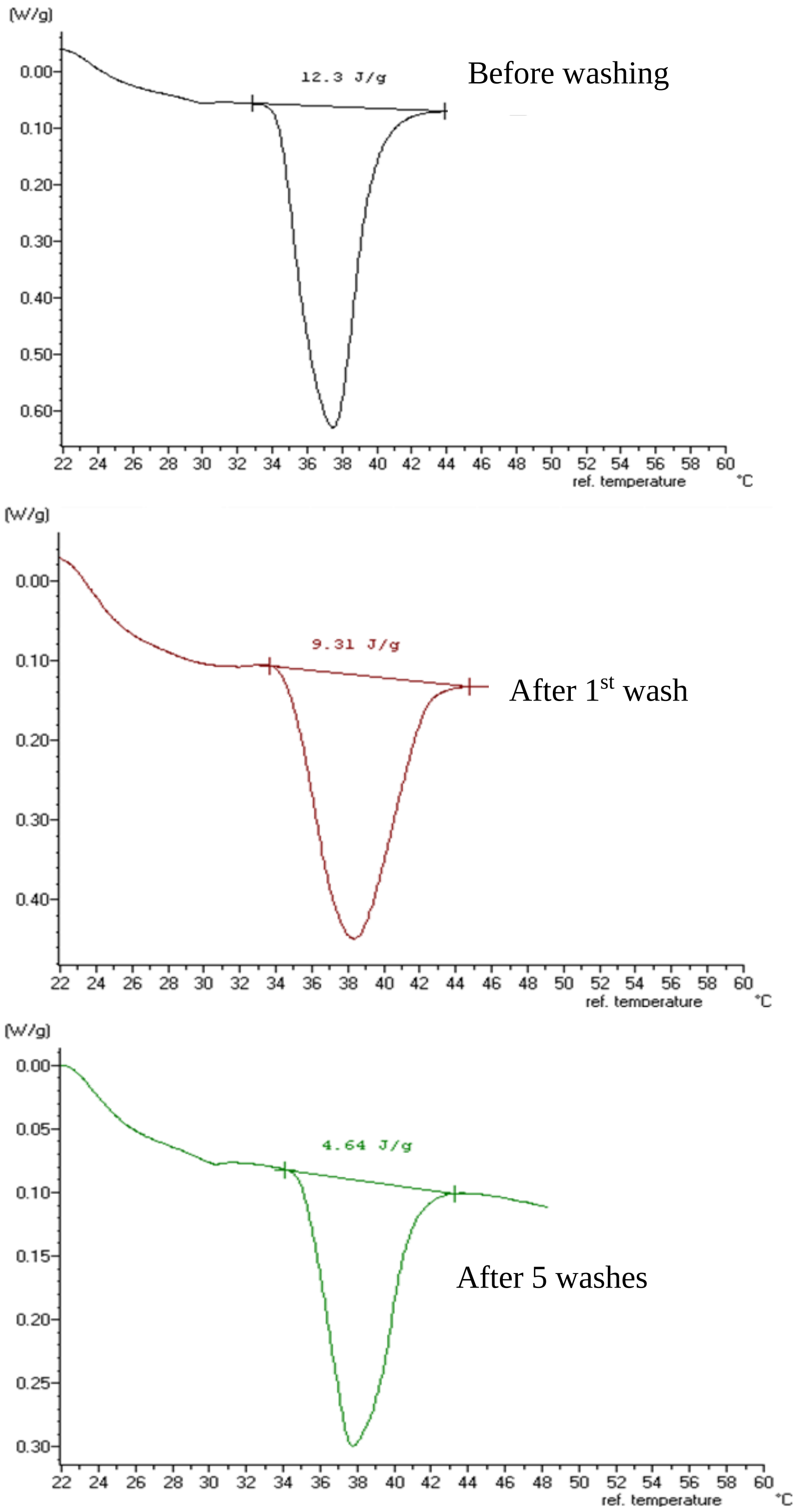

Figure 12 DSC graph of treated fabric after before and after washing

Comparison of synthesized nanocapsules with commercial microencapsulated PCM

The commercial microencapsulated PCM (paraffin) were also applied on textiles to compare the durability with synthesized nanoencapsulated Glauber’s salt. The comparison of fabrics’ latent heat with commercial microencapsulated PCM (paraffin) and synthesized nanoencapsulated Glauber’s salt before and after washing are shown in Figure 13. The capsules size is larger in case of microencapsulated PCM; therefore their attachment with fabric is weak. Therefore the loosely attached capsules are expelled during washing resulting in the decrease of latent heat. Figure 13 clearly shows that as the size of capsules decreases, their attachment with fabric increases via cross linking binder. Hence the latent heat of nanoencapsulated Glauber’s salt after washing is more as compared to the commercial MPCM because nano capsules are smaller in size and attach themselves with the fabric as an integral part of binder. Therefore nano range capsules perform better functionality when applied on fabric through pad application than the microcapsules.

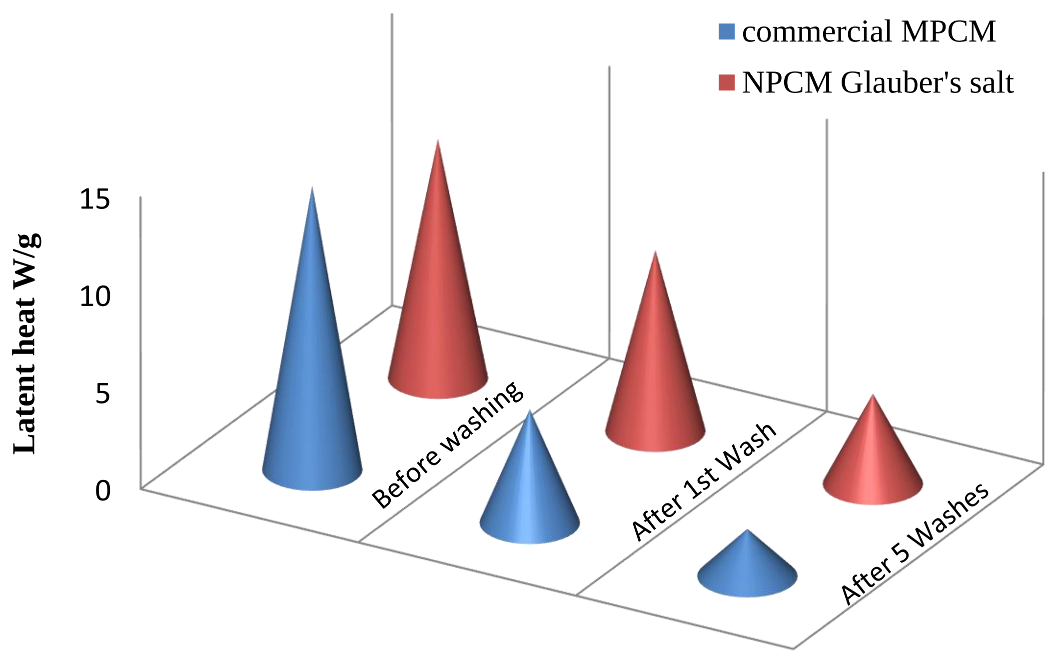

Figure 13 latent heat of fabric treated with commercial microencapsulated paraffin and synthesized nanoencapsulated Glauber’s salt

Conclusion

Glauber's salt was successfully encapsulated using PMMA shell and was characterized confirming the formation of capsules in the range of nano scale from 300 to 700 nm. The FTIR spectrum indicated that the nanocapsules contain Glauber's salt and PMMA as shell material. DSC results also indicated that the synthesized nanocapsules have phase change temperature closer to the human skin temperature. The nanocapsules were applied on fabric through pad application and showed better results as compared to the commercial microencapsulated phase change materials after multiple washings. This research also reveals that for better resistance to washing, the capsules to be applied should be in nano range and they will bound firmly with the fabric with the help of binder as its integral part.

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